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Existence of condensed phase in lattice gas model

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A three dimensional lattice gas model is considered, for investigations of thermodynamic properties of an assembly of particles, each of them comanding a rigid volume of exclusion. Dutta's lattice model (1953) for gases has been taken as the basis, and attempts have been made to deduce the equation of state. The possibility of existence of condensed phase in the lattice gas model has been examined by considering the distribution of particles in lattice points and by comparing the com[illegible]ssibility of two extreme cases. For simplicity, short range forces of very small range have been considered here.

1. INTRODUCTION

In 1953 it was shown by Dutta that the properties of the real gases and the distribution of the ions in the strong electrolytes in solutions might be deduced by quasi lattice theory. In the said quasi-lattice theory the particles (molecules, atoms, ions etc.) are distributed in a lattice. The distribution formula, deduced in this way for ions in strong electrolytes in solutions has been used in the theory of strong electrolytes. Later many author (e.g. Ruelle 1969, Fisher 1972 etc.) have worked on this model and they refer the structure as lattice gas. Ruelle (1969) called the lattice gas as a system constituted with hard cores which usually required that the Euclidian distance of each pair of particles remains larger than some constant (say, R) and so the configuration space is taken to be $3n$-dimensional with lattice points. Fisher (1972) also has taken the above structure of lattice gas in one dimension.

In the above work. It is found that the lattice theory is convenient for treating the matter in all the usual states i.e. solid, liquid gas. Attempts have been made to investigate the condensed phases and the phase transitions from the lattice gas model by the method of clusters (Temperley 1954, Ikeda 1974) and others (Neumann 1974). Neumann claimed that he solved the cooperative problem for a lattice gas on a simple cubic lattice by a system of two coupled, transcendental equations, derived by a combinatorial method. Actually he used the combinatorial method only to calculate the weight function which he had introduced in the partition function.

Here we show that by usual combinatorial method followed by maximising the thermodynamic probability and by the use of Boltzmann principle, the matter in gaseous phase and also in condensed phased, with the simple lattice gas model may be treated. A phase is identified as gaseous phase when the compressibility is comparatively high, whereas the same is identified as a condensed phase when the compressibility is very low, as good as incompressible. The phase transition has not been considered and is hoped to be studied in future. Only the existence of gaseous phase and condensed phase, in the sense explained above, have been demonstrated by applying combinatoric method with usual calculations.

Case 1. *Real gas in lattice model*

Lattice structure is convenient for treating real gas and in this section we have obtained the nature of the gas and have also calculated its compressibility, which has been compared with the compressibility obtained in Case II.

Description of the model

For investigation of certain properties of lattice gases it is essential to consider the distribution of the particles in a Euclidian space under the unilateral restriction $2a \leqslant |x_i - x_j|$. It is easy to show that (Ruell 1969), it is practically equivalent to the distribution of particles in three dimensional lattice points. In simple language the above distribution is equivalent to the distribution of particles on the lattice points and this model is generally referred to as lattice gas model. First we divide the whole space in a container in three dimensional lattice in such a way that the Euclidian distance between two points of the lattice must be equal to or greater than some constant, say $2a$ and also our assumption is that each lattice point may be occupied by only one particle. A pair of particles has only binding energy $2w$ if $2a \leqslant |x_i - x_j| < 2\sqrt{a2}$. Then we assume that the particles of only two types of which some are single particles and some are pair particles are distributed among the lattice points. Single particles are those type of particles around which nearest neighbours are vacant and so they have no potential energy, have only kinetic energy. Each of the particles of a particle-pair around which nearest cells are vacant has potential energy w along with its kinetic energy. Since for a single particle six nearest positions must be vacant, the effective exclusion volume for those type of particles is $b\left(=\frac{4}{3}(2a)^3\right)$, similarly the effective exclusion volume of particle pair is $b_2\left(=\frac{10}{3}(2a)^3\right)$. Let the effective exclusion volume of a particle-pair in presence of a single particle and of a single particle in presence of a particle pair be $\alpha_1 b_{12}$ where $\alpha_1 < 1$ and $b_{12} = b_1 + b_2$. These facts are clear from figure 1, which is the intersection of the lattice structure by a plane passing through central lattice.

Mathematical Calculations

Let the total volume be V, and so the total number of lattice points are $\frac{V}{b}$ where $b = \frac{4}{3}\pi a^3$. Let the total number of particles be N, the number of single particles be N_1 and the number of particle-pairs be N_2. Let a_i be the number of particles with kinetic energy ϵ_i. Let E be the total energy of the system.

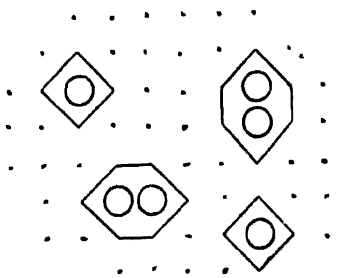

Fig. 1. Distribution of single particles and particle-pairs in lattice points.

The thermodynamic probability when the single particles are distributed first and then the particle pairs are distributed is

$$W_{12} = \frac{\left(\frac{V}{b_1}\right)!}{N_1!\left(\frac{V}{b_1}-N_1\right)!} \cdot \frac{\left(\frac{V-\alpha_1 b_{12} N_1}{b_2}\right)!}{N_2!\left(\frac{V-\alpha_1 b_{12} N_1}{b_2}-N_2\right)!} \cdot \frac{N!}{\pi a_i!} \quad \ldots (1)$$

Similarly, the thermodynamic probability when the particle-pairs are distributed first and then the single particles are distributed is

$$W_{21} = \frac{\left(\frac{V}{b_2}\right)!}{N_2!\left(\frac{V}{b_2}-N_2\right)!} \cdot \frac{\left(\frac{V-\alpha_1 b_{12} N_2}{b_1}\right)!}{N_1!\left(\frac{V-\alpha_1 b_{12} N_2}{b_1}-N_1\right)!} \cdot \frac{N!}{\pi a_i!} \quad \ldots (2)$$

Then the entropy S of the system (Cf. Dutta 1953, mixture of gases) is

$$S = \frac{k}{2}(\log W_{12} + \log W_{21}) \quad \ldots (3)$$

Using Stirling's formula in eq. (1) and (2) and then maximising the expression (3) under the following conditions

$$N_1 + 2N_2 = N \qquad \ldots (4.1)$$

$$\sum_i a_i = N \qquad \ldots (4.2)$$

$$\sum_i a_i e_i + 2N_2 w = E \qquad \ldots (4.3)$$

we get,

$$a_i = e^{-\lambda - \mu e_i} \qquad \ldots (5)$$

$$N_1^{2b_2} \cdot \frac{\left(\frac{V-\alpha_1 b_{12} N_1}{b_2}\right)^{a_1 b_{12}}}{\left(\frac{V-\alpha_1 b_{12} N_1}{b_2} - N_2\right)^{a_1 b_{12}} \left(\frac{V}{b_1} - N_1\right)^{b_2} \left(\frac{V-\alpha_1 b_{12} N_2}{b_1} - N_1\right)^{b_2}} = e^{-2b_2 \nu} \ldots (6)$$

$$N_2^{2b_1} \cdot \frac{\left(\frac{V-\alpha_1 b_{12} N_1}{b_2}\right)^{\alpha_1 b_{12}}}{\left(\frac{V-\alpha_1 b_{12} N_2}{b_1} - N_1\right)^{\alpha_1 b_{12}} \left(\frac{V}{b_2} - N_2\right)^{b_1} \left(\frac{V-\alpha_1 b_{12} N_1}{b_2} - N_2\right)^{b_1}} = e^{-2b_1(2\nu + 2\mu\omega)} \quad \ldots (7)$$

where n, μ, ν are Lagrange's undertermined multipliers. According to our model we can assume

$$\frac{N_1 b_1}{V}, \frac{N_2 b_2}{V}, \frac{\alpha_1 b_{12} N_1}{V}, \frac{\alpha_1 b_{12} N_2}{V} << 1$$

Using these approximations in (6) and (7) we get

$$N_1 = \left(\frac{V}{b_1}\right) e^{-\nu} \qquad \ldots (8)$$

$$N_2 = \left(\frac{V}{b_2}\right) e^{-2\nu - 2\mu\omega} \qquad \ldots (9)$$

Using eqs. (5), (8), and (9) in eq (3) we have

$$S = k \left[N(\nu + \lambda) + \mu E - N_1 \log\left(\frac{V}{b_1}\right) - N_2 \log\left(\frac{V}{b_2}\right) + N \log N + \right.$$

$$+ \frac{1}{2} \left\{ \left(\frac{V}{b_1}\right) \log\left(\frac{V}{b_1}\right) - \left(\frac{V}{b_1} - N_1\right) \log\left(\frac{V}{b_1} - N_1\right) + \right.$$

$$+ \left(\frac{V-\alpha_1 b_{12} N_1}{b_2}\right) \log\left(\frac{V-\alpha_1 b_{12} N_1}{b_2}\right) - \left(\frac{V-\alpha_1 b_{12} N_1}{b_2} - N_2\right)$$

$$\log\left(\frac{V-\alpha_1 b_{12}N_1}{b_2}-N_2\right)+\left(\frac{V}{b_2}\right)\log\left(\frac{V}{b_2}\right)-\left(\frac{V}{b_2}-N_2\right)\log\left(\frac{V}{b_2}-N_2\right)+$$

$$+\left(\frac{V-\alpha_1 b_{12}N_2}{b_1}\right)\log\left(\frac{V-\alpha_1 b_{12}N_2}{b_1}\right)-\left(\frac{V-\alpha_1 b_{12}N_2}{b_1}-N_2\right)$$

$$\log\left(\frac{V-\alpha_1 b_{12}N_2}{b_1}-N_1\right)\Big\}\Big] \qquad \ldots (10)$$

From the thermodynamic relation

$$\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_v$$

it follows

$$\mu=\frac{1}{kT} \qquad \ldots (11)$$

We get from eqs. (5) and (4.2)

$$\lambda=\log\left\{\frac{b}{Nh^3}\,(2\pi mkT)^{3/2}\right\} \qquad \ldots (12)$$

Finally, eqs. (8) and (9) leads to the following quadratic equation for e^{ν}:

$$2\left(\frac{V}{b_2}\right)\,e^{-\mu\omega}\,.\,e^{-2\nu}+\left(\frac{V}{b_1}\right)\,e^{-\nu}-N=0$$

the positive solution of which is (retaining upto second order of small quantity)

$$e^{-\nu}=\frac{Nb_1}{V}\left[1-\frac{2b_1}{b_2}\left(\frac{Nb_1}{v}\right)\,e^{-2\mu w}\right] \qquad \ldots (13)$$

and so $\nu=\log\left(\frac{V}{b_1}\right)-\log N-\log\left\{1-\frac{2b_1}{b_2}\,.\,\left(\frac{Nb_1}{V}\right)e^{-\frac{2w}{KT}}\right\}$ (Using (11))

From eqs. (8) and (9) N_0 and N_v become (using eqs. (11))

$$N_1=N\left[1-\frac{2b_1}{b_2}\,.\,\frac{Nb_1}{V}\,.\,e^{-\frac{2w}{KT}}\right]$$

$$N_2=\frac{b_1}{b_2}\,.\,\frac{N^2b_1}{V}\,e^{-\frac{2w}{KT}} \qquad \ldots (14)$$

Then putting eqs. (11), (12), (13) and (14) in eq. (10) the entropy becomes

$$S = k\left[\frac{E}{kT} + N\left\{\log\left(\frac{V}{b_1}\right) - \log N - \log\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right) + \log\left(\frac{b}{Nh^3}\right.\right.\right.$$

$$\left.\left.\left.(2\pi mkT)^{3/2}\right)\right\} + N\log N - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\log\left(\frac{V}{b_1}\right) - \frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot$$

$$e^{-\frac{2w}{kT}}\log\left(\frac{V}{b_2}\right) + \frac{1}{2}\left\{\left(\frac{V}{b_1}\right)\log\left(\frac{V}{b_1}\right) - \left[\frac{V}{b_1} - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]\log\left[\frac{V}{b_1}\right.\right.$$

$$\left.\left. - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right] + \left[\frac{V}{b_2} - \frac{\alpha_1 b_{12}}{b_2}N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]\right.$$

$$\log\left[\frac{V}{b_2} - \frac{\alpha_1 b_{12}}{b_2}N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right] - \left[\frac{V}{b_2} - \frac{\alpha_1 b_{12}}{b_2}N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\right.\right.$$

$$\left.\left.\times e^{-\frac{2w}{kT}}\right) - \frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]\times\log\left[\frac{V}{b_2} - \frac{\alpha_1 b_{12}}{b_2}N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right.$$

$$\left. - \frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right] + \left(\frac{V}{b_2}\right)\log\left(\frac{V}{b_2}\right) - \left[\frac{V}{b_2}\cdot\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]\log\left[\frac{V}{b_2} - \frac{b_2}{b_1}\right.$$

$$\left.\times\frac{N^2b_1}{V}e^{\frac{2w}{kT}}\right] + \left[\frac{V}{b_1} - \frac{\alpha_1 b_{12}}{b_1}\cdot\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]\log\left[\frac{V}{b_1} - \frac{\alpha_1 b_{12}}{b_1}\cdot\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\right.$$

$$\left.\times e^{-\frac{2w}{kT}}\right] - \left[\frac{V}{b_1} - \frac{\alpha_1 b_{12}}{b_1}\cdot\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\cdot N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]$$

$$\left.\times\log\left[\frac{V}{b_1} - \frac{\alpha_1 b_{12}}{b_1}\cdot\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}} - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]\right\}\right] \quad \ldots \quad (15)$$

$$\psi = S - \frac{E}{T} = k\left[N\left\{\log\left(\frac{V}{b_1}\right) - \log N - \log\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right.\right.$$

$$\left.\left. + \log\left(\frac{b}{Nh^3}(2\pi mkT)^{3/2}\right)\right\} + N\log N - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)$$

$$\log\left(\frac{V}{b_1}\right) - \frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\log\left(\frac{V}{b_2}\right)$$

$$+ \frac{1}{2}\left\{\left(\frac{V}{b_1}\right)\log\left(\frac{V}{b_1}\right) - \left[\frac{V}{b_1} - N\left(1 - \frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]\right.$$

$$\log\left[\frac{V}{b_1}-N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]+\left[\frac{V}{b_2}-\frac{\alpha_1 b_{12}}{b_2}N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]$$

$$\log\left[\frac{V}{b_2}-\frac{\alpha_1 b_{12}}{b_2}N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]$$

$$-\left[\frac{V}{b_2}-\frac{\alpha_1 b_{12}}{b_2}N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)-\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]$$

$$\times\log\left[\frac{V}{b_2}-\frac{\alpha_1 b_{12}}{b_2}N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)-\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]$$

$$+\left(\frac{V}{b_2}\right)\log\left(\frac{V}{b_2}\right)-\left[\frac{V}{b_2}-\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]\log\left[\frac{V}{b_2}-\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]$$

$$+\left[\frac{V}{b_1}-\frac{\alpha_1 b_{12}}{b_1}\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]\log\left[\frac{V}{b_1}-\frac{\alpha_1 b_{12}}{b_1}\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}\right]$$

$$-\left[\frac{V}{b_1}-\frac{\alpha_1 b_{12}}{b_1}\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}-N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]$$

$$\times\log\left[\frac{V}{b_1}-\frac{\alpha_1 b_{12}}{b_1}\frac{b_1}{b_2}\cdot\frac{N^2b_1}{V}\cdot e^{-\frac{2w}{kT}}-N\left(1-\frac{2b_1}{b_2}\cdot\frac{Nb_1}{V}\cdot e^{-\frac{2w}{kT}}\right)\right]\Bigg\}\Bigg] \quad \ldots \quad (16)$$

The thermodynamic relation

$$p=T\left(\frac{\partial\psi}{\partial V}\right)_T$$

leads to the equation of state of the system (retaining up to the second order terms of $\frac{Nb_1}{V}$ as $\frac{Nb_1}{V}<<1$)

$$p+\frac{\alpha}{V^2}=\frac{NkT}{V-\beta} \quad \ldots \quad (17)$$

where

$$\left.\begin{aligned}\alpha-\alpha(T)&=kN^2b_1{}^2T\left(\frac{3}{b_2}\cdot e^{-\frac{2w}{KT}}-\frac{1}{2b_1}\right)\\ \beta=\beta(T)&=\frac{2b_1}{b_2}\cdot Nb_1e^{-\frac{2w}{KT}}\end{aligned}\right\} \quad \ldots \quad (18)$$

The equation of state (17) is the same form as the van der Waal equation of state of real gas. The only difference is that in van der Wall's equation α and β are constant, but here α and β are funcions of temperature and the binding energy of particle-pairs.

From eq. (17) the compressibility for the above system is given by

$$x_1 = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\frac{NkTV}{(V-\beta)^2} - \frac{2\alpha}{V^2}} \quad \ldots (19)$$

Taking $\alpha = 1.42 \times 10^6$ atoms$\times$cm^4, $\beta = 41$ c.c. for a gram mole at N.T.P. of a van der Wall's gas (e.g. Argon) (Cf. Saha & Srivastava 1965) we have estimated the value of the exclusion volume b of a particle and the binding energy w of a pair-particle. The value of $b \sim 10^{-24}$ cm^3 which is actually happend to be of proper order. We have also calculated the compressibility by the formula (19) and it is shown that the compressibility $x_1 \sim 10^{-6}$ dynes cm^{-2} which actually occurs for a gas.

Case II : *Lattice gas model in condensed phase*

Here we have considered the general physical properties along with the compressibility of the system. Comparing the compressibility of this case with that of the former case we can see that it is much smaller than that obtained in Case I. Then, we can call this system a condensed phase.

Description of the model

In this case we also divide the whole space in a container into three dimensional lattice structure as explained in the former case. It is also assumed that each lattice sites can be occupied by only one particle. For this case our assumption is that most of all the lattice sites are occupied by particles and so the number of unoccupied lattice sites are very small as compared to that of occupied lattice sites. It is clear that possibilities of coming of two unoccupied cells (say, holes) in the two neighbou4ing sites is very small. The effective exclusion volume of a hole is $b_1\left(=\frac{4}{3}(2a)^3\right)$, which is the same as that in the former case. These are clear from the figure 2. which is the intersection of the three dimensional lattice model by a plane through the central lattice.

Mathematical Calculations

First we assume all the lattice points are filled up by the particles. Therefore, if $2w$ be the binding energy of two neighbouring particles, each particle has potential energy $6w$. Then we distribute among them few pseudo-particles with potential energy $-12w$, such that they contribute potential energy $-6w$ to the particles at their own positions so that they (say, holes) have potential

energy zero and also contribure potential energy $-w$ to the six neighbouring particles.

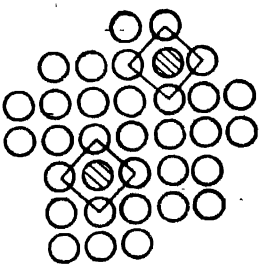

Fig. 2. Distribution of holes amongst particles.

Let V be the volume of the container and so the total number of lattice points are V/b, where $b = 4/3(\pi a^3)$. Let N be the number of particles, N_H be the number of holes. Let c_m be the number of particles with kinetic energy η_m. E be the total energy of the system. Then the thermodynamic probability is

$$W = \frac{\left(\frac{V}{b_1}\right)!}{N_H!\left(\frac{V}{b_1} - N_H\right)!} \cdot \frac{N!}{\prod_m c_m!} \qquad \ldots (20)$$

Using Stirling's approximation and taking logarithm of (20) we have

$$\log W = \left(\frac{V}{b_1}\right) \log \left(\frac{V}{b_1}\right) - N_H \log N_H - \left(\frac{V}{b_1} - N_H\right) \log \left(\frac{V}{b_1} - N_H\right) + N \log N - \sum_m c_m \eta_m \qquad \ldots (21)$$

Maximising log W under the conditions

$$\sum_m c_m = N \qquad \ldots (22.1)$$

$$\frac{V}{b} \cdot 6w - N_H \cdot 12w + \sum_m c_m \eta_m = E \qquad \ldots (22.2)$$

we have

$$c_m = e^{\lambda' - \mu' \eta_m} \qquad \ldots (23)$$

where λ', μ' are Lagrange's undetermined multipliers.

Since V/b is the total number of lattice points and N is the total number of particles and N_H is the number of holes, we have another condition :

$$\frac{V}{b} - N_H = N \qquad \ldots (24)$$

Inserting eqs. (23), (24) in eq. (21) and using the relation $S = k \log W$, we have the entropy,

$$S = k\left[\lambda' N + \mu' E - \mu'\left(12Nw - 6.\frac{V}{b}.w\right) + N\log N + \right.$$

$$+\left(\frac{V}{b_1}\right)\log\left(\frac{b}{b_1}\right) - \frac{V}{b}\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)\log\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)$$

$$\left. -\frac{V}{b}\left(1 - \frac{Nb}{V}\right)\log\left(1 - \frac{Nb}{V}\right)\right] \qquad \ldots (25)$$

As before we get

$$\mu' = \frac{kT}{1} \qquad \ldots (26)$$

and

$$\lambda' = \log\left\{\frac{b}{Nh^3}(2\pi mkT)^{3/2}\right\} \qquad \ldots (27)$$

Finally, the entropy is

$$S = k\left[N\left\{\frac{b}{Nh^3}(2\pi mkT)^{3/2}\right\} + \frac{E}{kT} - \frac{1}{kT}\left(12Nw - 6.\frac{V}{b}w\right) + \right.$$

$$+\left(\frac{V}{b_1}\right)\log\left(\frac{b}{b_1}\right) - \frac{V}{b}\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)\log\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)$$

$$\left. -\frac{V}{b}\left(1 - \frac{Nb}{V}\right)\log\left(1 - \frac{Nb}{V}\right)\right] \qquad \ldots (28)$$

Since

$$\psi = S - \frac{E}{T} = k\left[N\left\{\frac{b}{Nh^3}(2\pi mkT)^{3/2}\right\} - \frac{1}{kT}\left(12Nw - 6.\frac{V}{b}w\right) + \right.$$

$$+\left(\frac{V}{b_1}\right)\log\left(\frac{b}{b_1}\right) - \frac{V}{b}\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)\log\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right) -$$

$$\left. -\frac{V}{b}\left(1 - \frac{Nb}{V}\right)\log\left(1 - \frac{Nb}{V}\right)\right] \qquad \ldots (29)$$

Thus, the equation of state for this system is

$$p = kT\left[\frac{w}{kTb} + \frac{1}{b_1}\log\left(\frac{b}{b_1}\right) + \frac{1}{b}\left(1 - \frac{b}{b_1}\right)\log\left(\frac{b}{b_1} - 1 + \frac{Nb}{V}\right)\right.$$

$$\left. -\frac{1}{b}\log\left(1 - \frac{Nb}{V}\right)\right] \qquad \ldots (30)$$

From this equation of state we get the compressibility of this system. Since N_H are very small compared to the total number of lattice points, therefore, retaining up to the first order term of $\frac{N_H b}{V}$ i.e. $1-\frac{Nb}{V}$ the compressibility x_2 of this system is

$$K_2 = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{V}{NkT}\left(1-\frac{Nb}{V}\right) \tag{31}$$

Since $1-\frac{Nb}{V} \simeq 0$, comparing the expressions (19) and (31) we see that the compressibility in Case I is much larger than that in Case II Using the values of b and w estimated from Case I and taking $p = 50$ atoms, $T = -200°C$ (Since critical pressure and temperature are 48 atoms and $-122°c$ respectively for Argon) in (30) we calculate V and then by (31) we calculate the compressibility for this system. The compressibility $K_2 \sim 10^{-13}$ dynes cm^{-2}. One will be inclined to interpret it as a condensed phase.

3. Concluding remarks

We have discussed two extreme cases only to show that the lattice gas model is suitable for investigations of matter in the gaseous phase and in the condensed phase. It is to be noted that in our calculation in Case II we have got the compressibility very low even lower than the usually accepted value of condensed phase. In this connection it is to be noted that there are many intermediate cases where existence of particle-triplets, -quadruplets etc. may be frequent, but they are not considered here. It is naturally expected that in one of these cases quantitative agreement (at least in the order) may be obtained in the case of condensed phase. Moreover, when these intermediate possibility would be investigated a clear insight about the phase transition may be obtained.

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References

Dutta, M. 1953 *Proc. Nat. Inst. Sc. India*, **15**, 183.

Fisher, M. E. 1972 *Commun. Math. Phys.* **26**, 6.

Ikeda, K. and Nisizima, K. 1975 *Prog. Theo. Phys.* **53**, 326.

Neumann, H. P. 1974 *Z. Naurforsch* **29***a*, 65.

Ruelle, D. 1969 *Statistical Mechanics : Rigorous Results* W. A. Benjamin, Inc., New York.

Saha, M. N. and Srivastava, B. N. 1965 *A Treatise on Heat*, the Indian Press Privato Ltd., Allahabad.

Temperley, H. N. V. 1959 *Proc. Phys. Soc.* **74**, 183,